# PROCESS FOR MANUFACTURING SINGLE-WALL CARBON NANOTUBES

## Technical Field

The present invention relates to a process for manufacturing single-wall carbon nanotubes.

More specifically, the present invention relates to the preparation of nanoparticles (clusters) of carbon formed by nanotubes or nanofibers and particularly to the preparation of single-wall-nanotubes or SWNT.

## Background Art

Carbon nanotubes can be classified into two large categories: multiwall nanotubes and single-wall nanotubes. These two categories of nanotubes form two very different kinds of material in terms of structure and synthesis.

Multiwall carbon nanotubes comprise a plurality of single-wall carbon nanotubes arranged concentrically.

Nanotube physics is an interesting overlap of molecular physics along the transverse cross-section and of solid-state physics along the axis. In a manner similar to fullerene crystals, where the $C_{60}$ molecules can be arranged in an orderly manner to form a crystal, the nanotubes can be arranged in bundles of nanotubes (or nanotube strings).

Following the discovery of carbon nanotubes, important efforts have been made to synthesize them, particularly to synthesize single-wall carbon nanotubes, in view of their important applications.

A review of the applications of carbon nanotubes is provided by Baughman et al. [Baughman et al., Science 297, 787-792 (2002)]. Among these applications, it is worth mentioning the storage of hydrogen inside the tubes, the mechanical reinforcement of plastic materials ("nanocomposites"), nanoscopic and macroscopic actuators ("artificial muscles"), electrically conducting plastic materials for electrostatic dissipation for electromagnetic shielding, cold sources of electrons for light

emission devices (flat-panel displays), high-frequency microwave amplifiers, portable X-ray tubes, transparent electrodes for solar cells and light emission devices, vias and connectors for future-generation integrated circuits, resistors and capacitors integrated in loops of intelligent integrated circuits, vias, transistors and memory devices based on nanoelectronics.

High-quality single-wall nanotubes are required for fundamental and technological applications. The expression "high-quality nanotubes" is understood to reference nanotubes that have no chemical and structural defects or impurities or amorphous phases over a significant length along the axis of tube.

The processes currently used to prepare single-wall carbon nanotubes are based mainly on two techniques: laser ablation, which is a low-yield process that produces mainly single-wall nanotubes (the multiwall nanotube fraction can be a minority), and the Arc-Jet, which is a high-yield process that produces a mixture of nanotubes, mainly multiwall nanotubes, from which it is possible to extract single-wall nanotubes. Growth from the vapor phase instead is used to grow exclusively multiwall carbon nanotubes.

It should be noted that at present no process is known which produces exclusively single-wall nanotubes, whereas several processes for producing exclusively multiwall nanotubes are provided.

In the laser ablation process, laser pulses strike a graphite target with metallic catalysts in the presence of a hot stream of inert gas such as argon. When the carbon has vaporized, it mixes with an inert gas and then slowly condenses. The presence of a metal induces the formation of supersaturated droplets, from which single-wall carbon nanotubes (SWNT) grow. The purest SWNTs are produced by laser ablation of carbon containing metallic catalysts. The yield depends on the quantity and type of catalysts, on the power and wavelength of the laser, on the temperature, on the pressure and type of inert gas, and on the geometry of the fluid stream in the vicinity of the carbon target. Although it is possible to achieve an exceptionally high

quality of SWNTs grown in this manner, this technique has an important disadvantage, i.e., it allows only to produce fractions of a gram per hour. One should consider that the material that is collected contains up to 80% by weight of nanotubes, more than half of which is constituted by single-wall nanotubes. The difference is constituted by metallic particles, amorphous carbon and graphite. Moreover, the production costs of single-wall carbon nanotubes by using this technique are currently very high, currently approximately 1000 euros per gram, and this limits its possible applications.

The Arc-Jet technique, which is the most commonly used synthesis process for manufacturing carbon nanotubes, is based on the use of a plasma arc between graphite electrodes. The apparatus used in this technique is constituted schematically by a sealed container in which inert gas is made to flow and in which an electric arc is created between two graphite electrodes that contain suitable catalyst particles. The arc causes the evaporation of the graphite, which cools rapidly by making contact with the inert gas. A large amount of soot is thus produced which is constituted by nano- and microscopic particles of carbon, which are to a large extent amorphous. However, by adjusting the parameters of the process (arc power, pressure and flow of the gas, temperature), part of the formed material is constituted by carbon nanotubes, mostly of the multiwall type. By optimizing the composition, morphology and quantity of catalyst particles contained in the graphite electrodes, it is possible to synthesize an acceptable fraction of single-wall nanotubes.

The catalysts that are commonly used (also for the laser ablation process) are particles of iron, nickel, cobalt, yttrium and alloys thereof.

This technique produces relatively large quantities of low-purity material. The subsequent purification stages provide equally low yields with respect to laser ablation, which has comparable costs.

Finally, chemical vapor deposition (CVD) of hydrocarbons on

metallic catalysts is a classic process for producing carbon-containing materials. Various forms of carbon fiber, filaments and multiwall nanotubes have been synthesized by CVD.

The technique of ablation by pulsed electron beams, also known as Channel Spark Ablation (CSA), disclosed in US-5,576,593, has been used successfully to deposit various materials (mainly complex oxides) in the form of thin layers of extremely high purity.

The CSA system is based on generating, inside a hollow cathode, pulsed electron beams from the "glow-discharge" plasma environment. The electron pulse source is supplied by a bank of capacitors, charged by a 5-30 kV HT power supply. By switching an air gap switch or by means of another system capable of ionizing the gas at the base of the apparatus, the electron pulse is activated. The plasma in the hollow cathode generates an electron stream on the order of kA. The resulting electron beam is accelerated by the electrical field and exits, with a duration of 40-200 nanoseconds, through a dielectric channel in the anode deposition chamber.

Currently, the main applications of the CSA technique are high-temperature superconductor deposition and colossal magnetoresistance manganite deposition. In all these cases, the CSA technique provides a higher deposition rate, a better film quality and also a lower density of defects with respect to the expensive pulsed laser ablation technique. In all of the processes described so far, the CSA technique has been used to transfer directly the material of the target onto a substrate in the form of a thin film.

The formation of single-wall carbon nanotubes, however, has never been described by means of the CSA technique.

At present there are no synthesis processes that allow to obtain significant quantities of high-quality single-wall carbon nanotubes at competitive prices.

## Disclosure of the Invention

The aim of the present invention is to provide a process for producing single-wall and multiwall carbon nanotubes that also meets the set of requirements mentioned above.

A particular object of the present invention is to provide a process that allows to obtain carbon nanotubes in which the content of single-wall nanotubes is higher than the content of multiwall nanotubes.

Another object of the present invention is also to provide a process that is more simple and effective and has a lower energy consumption.

This aim and these and other objects are achieved, according to the present invention, by a process for preparing single-wall and multiwall carbon nanotubes by ablation, with pulsed electron beams, of a graphite target containing metallic catalysts.

Ways to carrying out the Invention

Conveniently, in the process according to the invention, a graphite target containing metallic catalysts, arranged within a reactor, is subjected to pulsed electron beams, in a stream of inert or hydrogen-containing and oxygen-free preheated gas, in order to produce the explosive evaporation of surface material of the target, said explosively evaporated material being conveyed by said gas stream through the reactor and optionally heated further.

However, it has been observed that, by subjecting to explosive evaporation (ablation) caused by pulses of electrons generated by a CSA system a target constituted by a mixture of graphite powder and particles of metallic catalyst according to the background art to produce carbon nanotubes with laser ablation or Arc-Jet techniques, part of the graphite that constitutes the target undergoes a structural transformation and, during the process of ablation, plasma formation and thermalization with the environment, condenses into nanostructured carbon aggregates and particularly into single-wall nanotubes and, to a far lesser extent, into multiwall nanotubes.

Surprisingly, it has been found that the pulsed electron beam ablation technique can be used to synthesize single-wall carbon nanotubes with good purity and homogeneity characteristics. The inherent yields of this deposition technique are high and exceed by more than one order of magnitude the yields obtained with laser ablation.

The deposition technique uses a tubular deposition reactor made of quartz or of another inert and refractory material, which is in communication with a system for generating pulsed discharges (channel-spark system) (provided as disclosed in US-5,576,793).

An inert gas (or a gas containing hydrogen in order to eliminate any traces of oxygen in the reaction area), preheated to 700-1200°, is made to flow in the reactor. Along the stream of gas, inside the reactor, a graphite target is provided that contains suitable catalyst metals according to the background art related to the two techniques mentioned earlier. Said target is struck by pulsed beams of electrons that arrive from the channel-spark system.

By acting appropriately on the electron acceleration energy, and particularly by working at energies below 10 kW, each electron pulse causes the explosive vaporization of the material arranged on the surface of the target. Said material, constituted by a mixture of ions, neutral atoms and clusters of variously ionized atoms, constitutes a so-called plasma plume at extremely high temperature (much higher than 1200°), which thermalizes with the gas stream kept at 700-1200° and is conveyed toward the area of the reactor where it is heated further.

This additional heating can be performed:

a) either by means of a heater with a tubular resistor arranged outside the reactor

b) or by means of a microwave pulse, optionally in phase relationship with respect to the electron pulse of the channel spark, released by means of an antenna that is arranged collectively with respect to

the reactor or by means of a waveguide arranged outside the reactor.

In the reactor, downstream of the heating area, a metallic surface is provided that is cooled appropriately to a temperature from 500° to 0° C (condenser) and on which the particles produced by the synthesis condense and can be collected.

An important aspect of the present invention is the system for adjusting the pressure inside the reactor and inside the channel-spark system, since these two parts of the system necessarily are in communication in order to allow the electron beam to exit from the discharge generator and strike the target arranged in the reactor.

As the gas pressure required to obtain carbon nanotubes in the reactor is much higher than the maximum pressure at which a correct electron pulse can form in the channel-spark system and accelerate against the target, it is necessary to apply a particular differential pumping system that is capable of maintaining a pressure differential of at least two orders of magnitude between the hollow cathode kept at $10^{-2}$ mbar and the volume that contains the target, which is kept at a pressure between 1 and 10 mbar.

In the present invention it is possible to operate with electron pulses at a relatively low energy level (lower than 10 kW).

However, it is possible to perform heating of the material that derives from the plasma of the plume very rapidly, to a temperature that cannot be determined but is higher than that of the inert carrier gas, (with the possibility to perform synchronization with respect to the electron pulse on the order of tens of nanoseconds and with a pulse duration ranging from tens of nanoseconds to tens of seconds) and very selectively (by utilizing the different absorption of microwaves by the molecular aggregates of carbon and metals that constitute the catalyst with respect to the carrier gas) by means of microwave pulses that are optionally synchronized with the electron pulses of the channel spark, where the term "synchronized" is used

in the sense of having the same frequency and a preset phase relationship with respect to them.

The process according to the present invention allows to obtain single-wall carbon nanotubes that have identical characteristics as regards purity, homogeneity and intrinsic characteristics with respect to those that can be obtained with laser ablation techniques. However, the obtainable yields are several orders of magnitude higher, because:

a) the yield (in terms of ablated material) per pulse (for an equal energy carried by a single pulse) is higher because of the higher efficiency of the energy release process on the part of the electrons with respect to the photons of the laser;

b) the pulse repeat frequency can be increased up to hundreds of hertz, against the tens of hertz that are typical of pulsed lasers that can be used for laser ablation;

c) the lower cost of the channel-spark system with respect to laser ablation systems, the lower energy consumption and the greater simplicity of the system allow, for an equal cost, the simultaneous use of at least three devices.

In order to ensure the necessary pressures in the two parts of the system (electron pulse generator and reactor) it is necessary to calibrate precisely the pumping rates by means of appropriate valves with an adjustable flow-rate, so as to keep the electron pulse generator at pressures below 5 $10^{-2}$ mbar regardless of the pressure in the volume of the reactor, which is kept above 1 mbar.

The integration of these fields with nanotubes is extremely attractive for many applications. The applicability of the CSA technique to the preparation of nanotubes resides in the high effective temperatures that can be reached on the surface of the targets and, as mentioned earlier, in the similarity of its performance with respect to the performance of pulsed laser ablation.

Example

Figure 1 illustrates the experimental layout used: the central part of a quartz tubular reactor 1 is heated by two electric high-temperature heaters 2, which maintain the temperature in the reactor at 1050 °C. As an alternative to the second heater, it is possible to use a microwave antenna 11. At the center of the reactor, in a downward region, an opening 3 allows the entry of the pulsed electron beams that arrive from a channel-spark source 4 (shown schematically), which is provided as disclosed in US-5,576,793. A needle valve 5 arranged at the left inlet of the reactor and two adjustable valves 6, 7, arranged respectively at the opposite end of the reactor and on the quartz neck 8 of the section that connects the reactor 1 to the spark to the channel-spark system 4, allow to maintain a flow of 5 normal cc/minute of argon in the reactor at a pressure of 1 mbar and a pressure of 2 $10^{-2}$ mbar in the CSA system. A target 9, constituted by a graphite disk containing 0.5 at% of Ni and 0.5 at% of Co is kept at an angle of 45°, at a height of 11-12 mm from the electron passage opening by a quartz support. By operating the channel-spark system at an acceleration voltage of 8-15 kV and at a pulse repetition frequency of 0.5-5 Hz, a sooty material is collected on the nanotube collector 10 (which is associated with a heat exchanger 12), which is constituted by a copper block inserted at the right end of the reactor by means of a sealed coupling and cooled in its part located outside the reactor by an air stream generated by a fan coil (temperature of the internal end of the collector <300 °C); said sooty material is constituted, in addition to amorphous carbon and graphite for a total fraction by weight of 15%, by carbon nanotubes, 65% of which is of the single-wall type.

The disclosures in Italian Patent Application No. MI2004A000008 from which this application claims priority are incorporated herein by reference.